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Periodic orbits of the hydrogen molecular ion

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Abstract. Based on our previous work [Yiwu Duan, J.M. Yuan, C.G. Bao, Phys. Rev. A **52**, 3497 (1995)], we study deeply the periodic orbits of the hydrogen molecular ion within the Born-Oppenheimer approximation (BOA). The Thiele-Burrau's transformation is introduced to regularize the singularities associated with the Coulomb potential terms and to transform the problem into a direct product of a pendulum and an anharmonic oscillator. This facilitates the analysis of the bifurcation properties of the periodic orbits. Some more details are also given about the calculation of the semiclassical density-of-state distribution using the Berry-Tabor formula.

PACS. 03.65.Sq Semiclassical theories and applications – 31.10.+z Theory of electronic structure, electronic transitions, and chemical binding

1 Introduction

The hydrogen molecular ion (H_2^+) within the Born-Oppenheimer approximation (BOA) is the simplest model for two- or multiple-centered systems, including all molecules. It was one of the systems that were closely examined around 1920's using the old and then newly developed quantum-mechanical methods [1]. However, good agreement between semiclassical and quantum treatments was not achieved until 1979, when Strand and Reinhardt [2] successfully applied the canonically invariant Einstein-Brillouin-Keller quantization method [3] to the H_2^+ system with uniform semiclassical corrections. It is well known that periodic orbits play an important role in the semiclassical quantization in the chaotic regime [4], in the understanding of discontinuities in chaotic scattering [5], in the theory of trapped trajectories [6] applicable to chemical reactions, resonances, and molecular spectroscopy [7], and in influencing the continuous Stark spectra of atomic hydrogen [8]. In view of their importance we have recently carried out a systematic study [9] of the periodic orbits of H_2^+ within BOA as a model for general two-centered problems. Our study of H_2^+ within and beyond BOA [9,10] are stimulated by the recent success of semiclassical treatments [11, 12] of doubly excited states of atomic helium, a three-body Coulomb system. In addition to Strand-Reinhardt's work, these recent investigations lend support to the usefulness of the classical treatment of electronic motion.

In our previous paper [9] we show that periodic orbits trace out loci in the classically allowed domains in the constant-of-motion parameter space. This picture formed by these curves in the constant-of-motion parameter space can also be considered as a bifurcation diagram for the periodic orbits, that is , a diagram which shows how periodic orbits are created or annihilated as parameters are varied. The allowed domains in the parameter space are classified into three regions [1,2], called P1, P2, and P3 by Strand and Reinhardt. We were not clear about the nature of bifurcations of the P2 and P3 orbits. The purpose of this paper is to show that the Thiele-Burrau regularization transformation [13] allows us to separate the system into two independent ones as well as regularize the dynamics. Under this transformation, the bifurcation behavior of the periodic orbits also becomes very clear.

The organization of the paper is as follows: We introduce the Thiele-Burrau transformation to regularize the equations of the H_2^+ system in Section 2. We then discuss the bifurcation properties of periodic orbits in Section 3. In Section 4, we present in more detail than reference [9] the semiclassical quantization of periodic orbits of the BOA H_2^+ system by calculating the density-of-states spectrum using the Berry-Tabor formula [14]. Some discussions of the dynamical behavior of H_2^+ beyond BOA are given in the last section.

2 Hamiltonian, equation of motion

The electronic part of the Hamiltonian for the planar H_2^+ within the Born-Oppenheimer approximation (BOA) is

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given by

$$H = \frac{p_x^2 + p_y^2}{2m_e} - \frac{Ze^2}{r_a} - \frac{Ze^2}{r_b}\,. \tag{1}$$

We assume the two protons are symmetrically placed on the x-axis with a distance R in between. This Hamiltonian in dimensionless variables becomes [1]

$$\mathcal{H} = \frac{p_x^2 + p_y^2}{2} - \frac{1}{r_a} - \frac{1}{r_b}\,. \tag{2}$$

A well-known treatment of the H_2^+ system is the introduction of the confocal ellipsoidal coordinates

$$\eta = (r_a - r_b)/R, \quad \xi = (r_a + r_b)/R\,. \tag{3}$$

In the η-ξ coordinates the Hamiltonian is

$$\mathcal{H} = \frac{2}{R^2(\xi^2 - \eta^2)}(H_\xi + H_\eta)\,, \tag{4}$$

where

$$H_\xi = (\xi^2 - 1)p_\xi^2 + 2R\xi, \quad H_\eta = (1 - \eta^2)p_\eta^2\,. \tag{5}$$

In this Hamiltonian still exist singularities at the points of $\xi = 1$ and $\eta = \pm 1$ (corresponding to electron-proton collision). Obviously we need another method to overcome this barrier. There are many other methods of regularization to remove the singularities within the three-body systems. One of the important methods is Thiele-Burrau's transformation [13]. Since the potential of a three-body Coulomb system is homogeneous, the dynamics is scale-invariant with respect to the energy or (in the BOA case) to the distance between the two protons R. For the H_2^+ under the BOA, we choose the later case, *i.e.*, we can set the scaled coordinate q and momentum p as: $q^{\rm sc} = q/R, p^{\rm sc} = \sqrt{R}p$, and $E^{\rm sc} = RE$. Thus, we may assume the distance $R = 1$. By introducing the new coordinates u and v as

$$r_a = \frac{1}{2}[\cosh(v) - \cos(u)], \quad r_b = \frac{1}{2}[\cosh(v) + \cos(u)]\,, \tag{6}$$

and a new time τ satisfying

$$\frac{{\rm d}t}{{\rm d}\tau} \equiv G(\theta) = r_a r_b = \frac{1}{8}[\cosh(2v) - \cos(2u)]\,, \tag{7}$$

the momenta p_u and p_v are related to p_x and p_y by

$$p_u = -\frac{\partial F_3}{\partial u} = -\frac{1}{2}[\sin(u)\cosh(v)p_x + \cos(u)\sinh(v)p_y]\,,$$
$$p_v = -\frac{\partial F_3}{\partial v} = \frac{1}{2}[\cos(u)\sinh(v)p_x - \sin(u)\cosh(v)p_y]\,, \tag{8}$$

where the generating function F_3 satisfies

$$F_3 = -[x(u,v)p_x + y(u,v)p_y] + Et\,. \tag{9}$$

Thus the momentum

$$p_x^2 + p_y^2 = \frac{1}{G(\theta)}(p_u^2 + p_v^2)\,, \tag{10}$$

and the regularized Hamiltonian becomes very simple:

$$\mathcal{K} = \frac{1}{2}(p_u^2 + p_v^2) - \cosh(v) - \frac{E}{8}[\cosh(2v) - \cos(2u)] = \frac{1}{2}(p_u^2 + p_v^2) + V(u,v) \equiv 0\,. \tag{11}$$

Clearly there is no singularity of the new Hamiltonian $\mathcal{K}$ in the whole u-v space, and the transformed Hamiltonian has an effective potential energy $V(u,v)$. In the u-v plane the equations of motion are

$$\dot{u} = \frac{{\rm d}u}{{\rm d}\tau} = p_u\,,$$
$$\dot{p}_u = \frac{{\rm d}p_u}{{\rm d}\tau} = \frac{E}{4}\sin(2u)\,, \tag{12}$$

and

$$\dot{v} = \frac{{\rm d}v}{{\rm d}\tau} = p_v\,,$$
$$\dot{p}_v = \frac{{\rm d}p_v}{{\rm d}\tau} = \sinh(v) + \frac{E}{4}\sinh(2v)\,. \tag{13}$$

The equation for u is just that of a pendulum and that for v is an anharmonic oscillator which may have symmetrical double well when E is fixed. This will provide us with a clear physical picture to understand the dynamics of the two-center Coulomb systems. On the other hand, it is easy to carry out the classical calculation by using the new Hamiltonian with no singularity.

It is well known that both the Hamilton-Jacobi equation and the Schrödinger equation are separable. Besides the total energy, a second constant of motion exists. It is easy to obtain this constant of motion given by

$$\Omega = p_u^2 - \frac{R^2 E}{2}\cos^2 u \left[= \left(p_\eta^2 - \frac{R^2 E}{2}\right)(1 - \eta^2)\right]\,. \tag{14}$$

This constant of motion is related to the Runge-Lenz vector of the Kepler problem and can be given by another form:

$$\Omega = \mathbf{L}_a \cdot \mathbf{L}_b + \frac{mRZe^2}{2}(\cos\theta_a - \cos\theta_b)\,. \tag{15}$$

Strand and Reinhardt [2] take the second constant of motion to be

$$G = -H - \frac{2\Omega}{mR^2}\,. \tag{16}$$

In these equations, $\mathbf{L}_i$ is the angular momentum vector of the electron about the proton i and the θ_i is the angle between the vector $\mathbf{r}_i$ and the x-axis, where i denotes the proton a or b. We denote below by γ the value of G scaled by Ze^2/R.

3 Periodic orbits and their bifurcations

It has been shown by Pauli and later Strand and Reinhardt [1,2] that all planar trajectories on tori can be classified into three types: P1, P2 and P3, and each type of

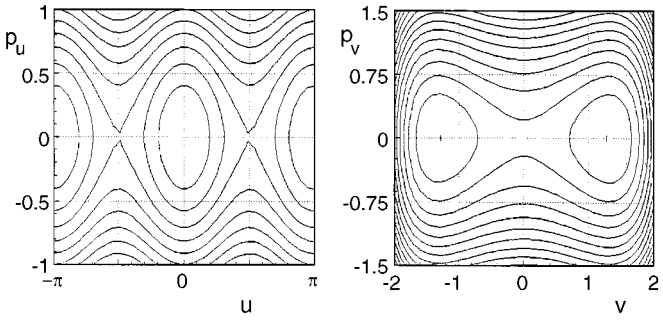

Fig. 1. Poincaré Surface of Section. Left: (p_u, u) and right: $(p_v.v)$ with $E = -1$.

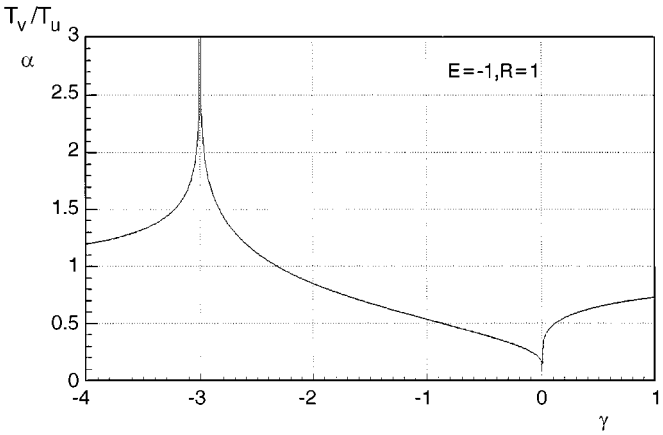

Fig. 2. Winding rate α as a function of γ with $E = -1$.

motion occupies a well-defined region in the parameter γ and E space. For the type P1 trajectory, the electron moves around the two protons between two ellipses and cannot cross between the protons; for type P2, its motion is inside a single ellipse and for type P3 the electron moves in a region localized around a single proton.

Under Thiele-Burrau's transformation, the classical dynamics becomes very clear. Let us start from the Poincaré Surface of the Section (PSOS). The PSOS can be directly obtained by rewriting the momenta p_u, p_v in terms of the two constants of motion γ and E as the follows:

$$p_u = \pm\sqrt{-\frac{1}{2}(\gamma + E\cos^2 u)}\,,$$
$$p_v = \pm\sqrt{2\cosh(v) + \frac{E}{4}\cosh(2v) + \frac{1}{4}(2\gamma + E)}\,. \quad (17)$$

In Figure 1 we present the PSOS with the energy fixed at -1 in the forms of $p_u - u$ and $p_v - v$, separately. From Figure 1 one may obtain the periods of u and v motion as

$$T_u = \oint \sqrt{\left(-\frac{1}{2}(\gamma + E\cos^2 u)\right)^{-1}}\,\mathrm{d}u\,,$$
$$T_v = \oint \sqrt{\left(2\cosh(v) + \frac{E}{4}\cosh(2v) + \frac{1}{4}(2\gamma + E)\right)^{-1}}\,\mathrm{d}v. \quad (18)$$

Thus the winding number α of a trajectory is just the ratio of T_u and T_v

$$\alpha \equiv \frac{T_u}{T_v}\,. \quad (19)$$

In Figure 2 we give the winding rate α as a function of the constant of motion γ with $E = -1$. The general orbit is quasiperiodic. Only when the winding number is a rational fraction m/n a periodic orbit occurs. The periodic orbits have been presented in reference [9] and we will not discuss them in this paper. Instead, we present here some typical high-period orbit with the self-similarity inside such a separable system in Figure 3. If we fix α at a definite rational fraction, and let the parameters γ and E vary, we then obtain a curve corresponding to a periodic orbit with winding number α in the parameter space. We present some curves of periodic orbits in the parameter space in Figure 4. In reference [9] we have studied the convergent properties of the periodic orbits. Here we would like to give a brief report of these properties.

(i) The sequences of type P1, can be represented by $\alpha = n : m$ with m fixed and n going to infinity and converge to the boundary separating the P2 and P1 domains. The limiting periodic orbit, denoted by $\infty : 1$, corresponds to the intercenter-line connecting the two protons ($v = 0$). Actually, this orbit is the shared limiting orbit of both the sequences of the P1 and P2 orbits. From Figure 4 we know that the sequence of curves representing the $1 : 2n$ orbits of P2 types converges onto the boundary separating the P2 and P3 types. The boundary is just the periodic perpendicular to the internuclear axis, with the winding number, $1 : \infty$ ($\eta = 0$ or $u = \pm\frac{\pi}{2}$). This orbit was called [1] saddle orbit for it goes through the saddle point of the potential. Within the P2 domain of the parameter space, the sequences of orbits with $\alpha = m : 2n$, where m is fixed and n approaches infinity, will converge onto the boundary saddle orbit as n increases. The saddle orbit is also the limiting orbit of the sequences for the P3 periodic orbit with winding number $\alpha = m : n$ as n increases (m is fixed).

(ii) Besides convergent properties of the periodic orbits, Figure 4 also tell us about the bifurcation properties of periodic orbits, that is, it functions as a bifurcation diagram, in which we show how periodic orbits are born or annihilated as we vary a control parameter, such as energy or γ. Each curve in Figure 4 represents the existence of periodic orbit of a certain winding number at certain values of constants of motion. More accurately, each point on the curve corresponds to the existence of a rational torus, thus of an infinite number of periodic orbits. Focusing first on the P1 domain (0ACB) of the parameter space, we see that all P1 orbits bifurcate from the AC curve, its boundary with the forbidden region. This curve actually represents the $1 : 0$ orbit, an ellipse, which is stable when the energy is greater than -2.

To get a completed picture of the bifurcation, We carry out our analysis of stability of the mother orbit through the calculation of the monodromy matrix. Consider a

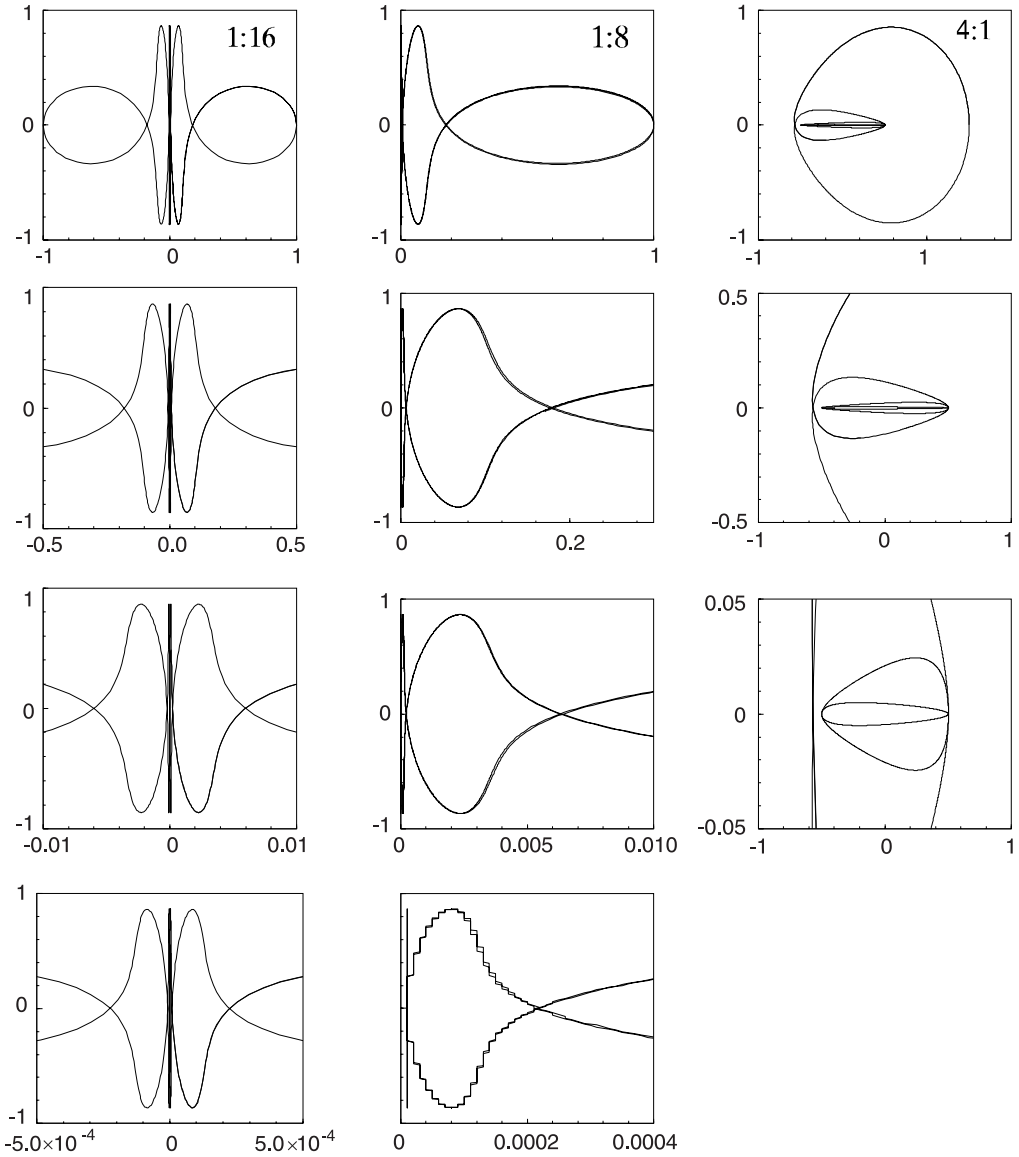

Fig. 3. Some examples of the self-similarity within high-period orbits. Left: the 1:16 orbit of type P2, centre: 1:8 of P3 and right: 4:1 of type P1.

periodic orbit with period T as

$$x^*(T) = x^*(0)\,, \tag{20}$$

where x denotes both (u, v) and (p_u, p_v). Let a displacement $\delta x(t)$ occur. Thus from the equations of motion (eqs. (12) and (13)) we obtain

$$\begin{aligned} \delta\dot{q}_i &= \delta p_i\,, \\ \delta\dot{p}_i &= -\delta(\frac{\partial V}{\partial q_i}) = -\frac{\partial^2 V}{\partial q_i \partial q_j}\delta q_j = -V_{ij}\delta q_j\,. \end{aligned} \tag{21}$$

These equations can be written in the matrix form as

$$\delta\dot{x}(t) = H''(t)\delta x(0)\,, \tag{22}$$

where

$$\delta\dot{x} = (\delta q_1, \delta p_1, \delta q_2, \delta p_2)^T\,, \tag{23}$$

and

$$H'' = \begin{bmatrix} 0 & 1 & 0 & 0 \\ -V_{11} & 0 & -V_{12} & 0 \\ 0 & 0 & 0 & 1 \\ -V_{21} & 0 & -V_{22} & 0 \end{bmatrix} =$$

$$\begin{bmatrix} 0 & 1 & 0 & 0 \\ \frac{E}{2}\cos(2u) & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & \cosh(v) + \frac{E}{2}\cosh(2v) & 0 \end{bmatrix}. \tag{24}$$

From the definition of the monodromy matrix:

$$\delta x(T) = M(T)\delta x(0) \tag{25}$$

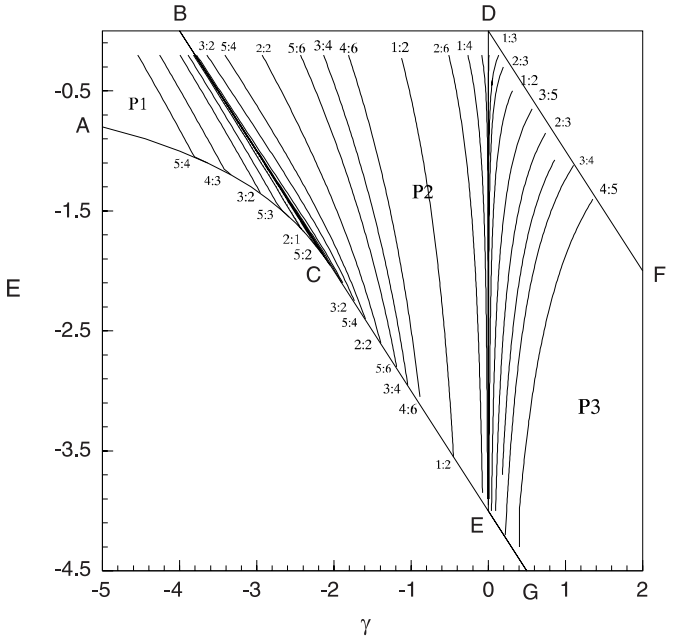

Fig. 4. Curves representing existence of periodic orbits in the $\gamma - E$ parameter space. These curves are labeled by the winding numbers of the periodic orbits. The BCED domain represents the region for type P2, the region to its left (0ACB) corresponds to type P1 and that to its right to type P3.

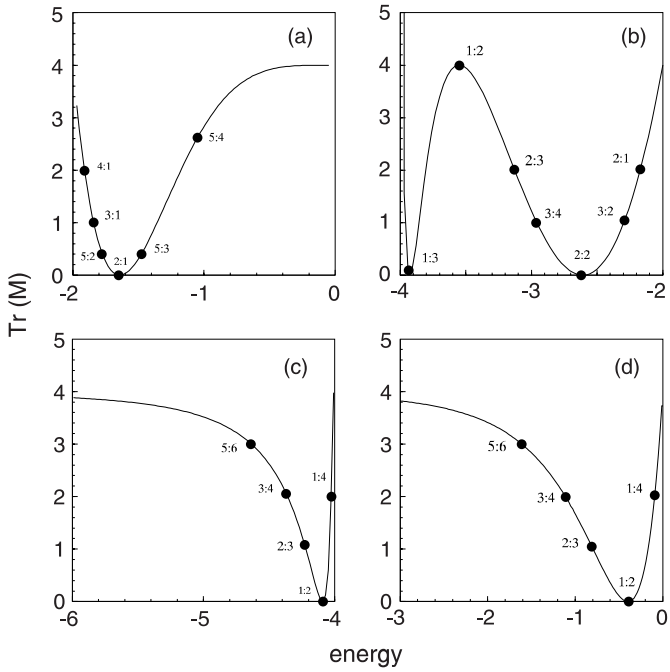

Fig. 5. Bifurcations of the periodic orbits of BOA H_2^+. The curves are the traces of the monodromy matrix as a function of E. (a) The trace of the elliptic orbit of P1 type. (b) That of the inter-nuclear orbit of P2. (c) The trace of the borderline orbit of EG in Figure 2 and (d) borderline DF orbit of type P3. As energy decreases, when the trace goes through (a) $2 + 2\cos(\pi/\alpha)$; (b) $2 + 2\cos(2\pi/\alpha)$; (c) and (d) $2 + 2\cos(2\pi\alpha)$, with α is a rational number, the corresponding rational torus and its embedded periodic orbit bifurcates out of the mother orbits. Symbols indicate the bifurcation energies of the orbits.

and equation (22) we have

$$\delta\dot{x}(T) = \dot{M}(T)\delta x(0) = H''(T)\delta x(T) = H''(T)M(T)\delta x(0). \quad (26)$$

Thus the evaluation equation of the monodromy matrix is

$$\dot{M}(T) = H''(T)M(T)\,, \quad (27)$$

with $M(0) = I$.

The trace of the matrix for the $1:0$ orbit is shown in Figure 5(a). As energy varies, the trace of the monodromy matrix of this elliptic periodic orbit changes too. When its value goes through $2 + 2\cos(2\pi/\alpha)$, where $\alpha = m:n$ and m and n are integers, a periodic orbit of the winding number α bifurcates from it. As energy approaches to -2, the trace of the monodromy matrix goes to 4 sharply, and the elliptic orbit will become unstable. This bifurcation route is in exact analogy with the one observed for the system of atomic hydrogen in the presence of electric field [8]. If we investigated the bifurcation of the periodic orbits of types P2 and P3 in the xy-coordinates or the $\eta\xi$-coordinates, the situation seems more complicated. In the P2 domain, curve AC merges onto the straight line BG (at point C), which corresponds to the borderline, $\alpha = \infty : 1$, orbit. As the periodic orbits approach this boundary with the forbidden region from the high-energy side, these orbits change shape gradually and resemble more and more closely the inter-center orbit in many aspects except that the maximal values of their p_y components approach infinity, while that of the inter-center orbit remains zero. Similar relation exists between the P3 periodic orbits and the borderlines, EG and DF, which correspond also to the periodic orbits lying on the x-axis. The x-axis orbits, however, consist of four pieces, separated by the proton and the inter-proton potential barrier, in the P3 domain. Because of this,in our previous paper [9] we are not able to make an analysis on the bifurcation of the P2 and P3 types.

Under Thiele-Burrau's transformation, the calculation of the monodromy matrix can be run with no singularities. Figure 5(b) shows the trace of the monodromy matrix for the internuclear orbit from which all P2 orbits bifurcate. When its value goes through $2 + 2\cos(\pi/\alpha)$, (not $2 + 2\cos(2\pi/\alpha)$, because of the two potential wells for $-\pi \le u \le \pi$), a new P2 periodic orbit of winding number α bifurcates from it. As energy approaches to -4, the trace of the monodromy matrix goes to infinity sharply, and the orbit becomes very unstable. A similar situation exists in the P3 domain. The traces of the monodromy matrices for the borderline orbits EG and DF are plotted in Figures 5(c) and (d), respectively. Again, when the trace goes through $2 + 2\cos(2\pi\alpha)$, a new P3 orbit with winding number α is born from the upper or lower borderline orbits.

It should be pointed out that all the orbits are stable in general, including the mother orbit itself. The special case is the saddle orbit, which is always unstable. The

saddle orbit and the inter-nuclear orbit merge at point E (see Fig. 4) where the total energy equals to -4 and the period of the pendulum for the variable u becomes infinity at this energy corresponding to a hyperbolic point at $E = -4$ of equation (14). This is why the trace of the monodromy matrix approaches to infinity sharply at this point. Similar situations occur in the borderline orbit of P1 and P2 types.

4 Semiclassical quantization

The H_2^+ system, like He, is considered to be one of the fundamental quantum-mechanical systems. It has been shown that the periodic orbits of the helium atom could tell us its quantum properties, and now the problem of the semiclassical quantization of the periodic orbits of H_2^+ becomes more important. Based on Feynman's path integrals Gutzwiller expresses the density of states in terms of periodic orbits in his now famous trace formulas [4]. There are several versions of trace formulas, all derived based on similar main ideas, that is, we can obtain a semiclassical expression for the density of states by taking the trace of a semiclassical approximation of Green's function. For the latter, we can use the Fourier transform of a generalized Van Vleck propagator and evaluate all integration involved by the stationary phase approximation. An application of this procedure to integrable systems (including separable systems) generates a trace formula, which turns out to be identical to a semiclassical expression obtained by Berry and Tabor [14], who are the first to derive such a formula for integrable systems. The procedure employed by Berry and Tabor [14] makes it clear that their formulas apply rigorously only to integrable systems, because in the derivation they replace the energy in the density of state equation by an expression given by the EBK quantization rules.

The trace formula derived by Gutzwiller for hard chaos can be extended to include stable periodic orbits [4] and thus are sometimes used for mixed systems. In deriving this version of the trace formula, it was assumed that the periodic orbits are isolated. This assumption is certainly not valid for separable systems, because there are continuous distributions of periodic orbits on rational tori in these systems.

Since the present system is separable, we have used the Berry-Tabor formula for the calculation of the density of states. For a two-dimensional system with spherical potential $V(r)$, Berry and Tabor obtained the density-of-state formula as

$$n(E) = n_{\mathrm{TF}}(E) + \frac{2}{\sqrt{\pi}\hbar^{3/2}} \sum_{M_S} \sum_{M_L} \frac{\epsilon(\mathbf{M})\tau(L_M, E)}{\sqrt{M_S \dfrac{\partial \Theta(L_M)}{\partial L}}} \times \cos\left[\frac{W(\mathbf{M})}{\hbar} - \left(M_S + \frac{1}{4}\right)\pi\right], \tag{28}$$

where $n_{\mathrm{TF}}(E)$ is the Thomas-Fermi term, and

$$\tau(L_M, E) = \frac{\partial S(L, E)}{\partial E}, \qquad \Theta(L_M) = -\frac{\partial S(L, E)}{\partial L} \tag{29}$$

with

$$S = \int_{r_1}^{r_2} \sqrt{2m\left(E - V(r) - \frac{L^2}{2mr^2}\right)}\mathrm{d}r\,. \tag{30}$$

In these equations, $W(M)$ is the action around a closed orbit, $\mathbf{M} = (M_S, M_L)$ the topological lattice vector, and $\epsilon(M)$ is a degeneracy fractor equal to two if $M_L \neq 0$ and unity if M_L=0. Based on this formula, using the separable coordinates ξ and η, the H_2^+ system resembles closely a spherical potential system, in which we set $\eta = \cos\theta$ and the associated action relates directly to the angular momentum, we then obtain

$$n(E) = n_{\mathrm{TF}}(E) + \frac{2}{\sqrt{\pi}\hbar^{3/2}} \sum_{m_\xi} \sum_{m_\eta} \frac{\epsilon(\mathbf{M})\tau(L_M, E)}{\sqrt{m_\xi \dfrac{\partial \Theta(L_M)}{\partial L}}} \times \cos\left[\frac{W(\mathbf{M})}{\hbar} - \left(m_\xi + \frac{1}{4}\right)\pi\right], \tag{31}$$

where m_η and m_ξ are the number of cycles in the η coordinate and that in the ξ coordinate, and

$$S = \int_{\xi_{\min}}^{\xi_{\max}} \sqrt{2m_e\left(\frac{R^2E}{2} + \frac{2R\xi}{(\xi^2-1)} - \frac{\Omega}{2m_e(\xi^2-1)}\right)}\mathrm{d}\xi\,, \tag{32}$$

where $\xi_{\min}$ ($\xi_{\max}$) is the minimum (maximum) of the variable ξ determined by the energy E, γ, and the type of orbit:

$$\xi_{\max} = -\frac{2}{E}\left(1 + \frac{1}{2}\sqrt{4 - \gamma E}\right), \tag{33}$$

$$\xi_{\min} = \begin{cases} -\dfrac{2}{E}\left(1 - \dfrac{1}{2}\sqrt{4 - \gamma E}\right) & \text{for P1 orbits,} \\ 1 & \text{for P2 and P3 orbits,} \end{cases} \tag{34}$$

and the Thomas-Fermi term is

$$n_{\mathrm{TF}}(E) = \left(\frac{m_e}{2\pi\hbar^2}\right)^{\frac{3}{2}} \frac{1}{\Gamma(3/2)} \int_{-1}^{1} \mathrm{d}\eta \times \int_{\xi_{\min}}^{\xi_{\max}} \sqrt{\frac{E(\xi^2 - \eta^2) + 4\xi}{R(\xi^2 - \eta^2)}}\mathrm{d}\xi\,. \tag{35}$$

According to Berry and Tabor's derivation, the density-of-state for a three-dimensional system with similar potential are the same as that for a two-dimensional system except

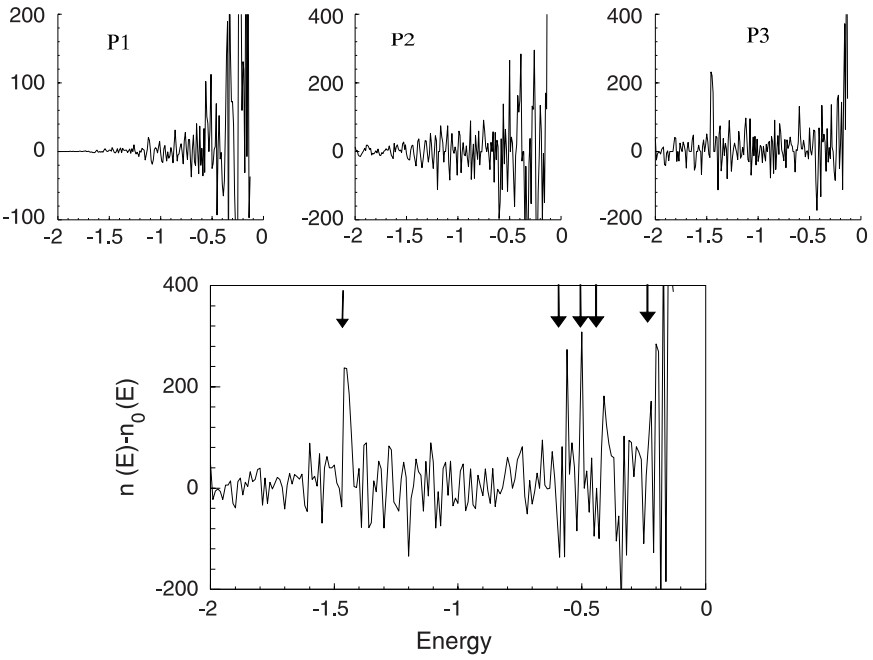

Fig. 6. Semiclassical density of states distribution, $n(E)$, and the exact quantum eigenvalues (denoted by arrows) of the H_2^+ ion. The upper three pictures are the distributions from the P1, P2 and P3 types, respectively. The lower one includes all the three types. $n_0(E)$ represents the Thomas-Fermi distribution which is almost zero except when E is very close to zero.

for the degeneracy fractor

$$\epsilon(M) = \frac{2L_M}{\hbar} = (2m_\eta + 1)\,. \tag{36}$$

We would like to emphasis that the above semiclassical quantization equations could be derived to be similar forms in the u-v plane.

After successfully fitting properties of periodic orbits, such as actions, periods, curvatures and especially the relationship between γ, E, and α, we have included in our calculation of the density of states all periodic orbit of $\alpha = p : q$ with p and q not exceeding 40, and orbits of all three types. It means that we have used thousands of periodic orbits in our calculation and the results for $R = 1$ bohr are presented in Figure 6. It is obvious that the agreement between the semiclassical density of states distribution with the exact quantum eigenenergies is reasonably good, especially for the few lowest states. Since we have employed scaled phase space, one may find the results for the other distance $R \neq 1$ by setting the Planck constant as $\hbar^{\rm sc} = \hbar/\sqrt{R}$ in equations (31, 36), or obtain the semiclassical quantized energy directly by $E = E^{\rm sc}/R$. The results for the other distance are not so good as that for the distance $R = 1$ because of the limitation of the primitive semiclassical quantization. Unlike the frozen planet configuration of He, the electron tunneling through the potential barrier plays an important role in the semiclassical quantization of the hydrogen molecular ion. Thus significant improvements can only be expected when we go beyond the primitive semiclassical quantization methods(the details for this problem can be found in recent papers [10,16]).

5 Discussions

Considering the fact that the H_2^+ has been believed to be a well-understood system, our exhaustive work on semiclassical quantization will add, of course, the fundamental knowledge to this system. The orbits we found are important, for they are prototype periodic orbits for a two- or multiple-centered systems and may play roles in the classical understanding of chaotic scattering and, possibly, the chemical bonding associated with these system. For the latter aspect we have carried out a first study in [9,10]. Mueller, *et al.* [15] have also recently reexamined the classical stability problem of H_2^+ beyond BOA and found the approximate adiabatic invariant of the system. However, up to now the classical dynamical behavior of H_2^+ beyond BOA has not been fully explored. In reference [10] we treat the motions of electron and the two protons on the same footing and find that the type P2 orbits change to be motions on torus in the non-BOA case, and types P1 and P3 orbits become chaotic. Besides these, we also find a hybrid motion between types P2 and P3, and the H_2^+ system with this hybrid motion is still bond. The hybrid motion is important in the Non-BOA H_2^+ and may suggest a new type of chemical bonding or electronic state, which can not be described accurately within the BOA.

As stated earlier, the bifurcation patterns of H_2^+ resemble closely that of atomic hydrogen in an electric field, another separable system. For the latter system, the periodic orbit bifurcation may manifest themselves in the spectra of H_2^+. It would be interesting to predict theoretically the related signatures in the molecular spectra.

Finally, with all the interesting periodic orbits unearthed, important questions follow. One which rises to

the fore is whether or not any of these orbits continue to exist when the protons are allowed to move and how their stabilities change with the types of nuclear motions *i.e.*, rotation, vibration, and both. Among the possibilities are: torus behavior replaces a periodic orbit, a periodic orbit changes stability, a periodic orbit disappears, new types of periodic orbits and chaotic trajectories emerge etc. These tori or periodic orbit structures may be useful for understanding the properties of long-range van der Waals states of the H_2^+ system.

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References

1. W. Pauli, Ann. Phys. (Leipzig) **68**, 177 (1922).
2. M.P. Strand, W.P. Reinhardt, J. Chem. Phys. **70**, 3812 (1979).
3. G.S. Ezra, C.C. Martens, L.E. Fried, J. Phys. Chem. **91**, 3721 (1987).
4. M.C. Gutzwiller, *Chaos in Classical and Quantum Mechanics* (Springer-Verlag, New York, 1990).
5. B. Eckhardt, Physica D **33**, 89 (1988).
6. E. Pollak, P. Pechukas, J. Chem. Phys. **69**, 1218 (1978).
7. O. Hahn, H.S. Taylor, J. Chem. Phys. **96**, 5915 (1992).
8. J. Gao, J.B. Delos, Phys. Rev. A **49**, 869 (1994); M. Courtney, H. Jiao, N. Spellmeyer, D. Kleppner, J. Gao, J.B. Delos, Phys. Rev. Lett. **74**, 1538 (1995).
9. Yiwu Duan, J. M. Yuan, C.G. Bao, Phys. Rev. A **52**, 3497 (1995).
10. Yiwu Duan, C. Browne, J.M. Yuan, Phys. Rev. A **59**, 238 (1999).
11. J.M. Yuan, D.H. Feng, G.M. Zaslavsky (Editors), *Quantum Dynamics of Chaotic Systems* (Gordon and Breach, Amsterdam, 1993).
12. K. Richter, G. Tanner, D. Wintgen, Phys. Rev. A **48**, 4182 (1993); G.S. Ezra, K. Richter, G. Tanner, D. Wintgen, J. Phys. B **24**, L413 (1991); R. Blumel, W.P. Reinhardt in *Quantum Nonintegrability: Directions in Chaos*, Vol. **4**, edited by D.H. Feng, J.M. Yuan (World Scientific, Singapore, 1992), p. 245; J. Mueller, J. Burgdoerfer, D.W. Noid, Phys. Rev. A **45**, 1471 (1992).
13. T.N. Thiele, Astron. Nachr. **138**, 1 (1896); C. Burrau, Vierteljahrsschrift Astron. Ges. **41**, 261 (1906); V. Szebehely, *Theory of Orbits* (Academic, New York, 1967), chapt. 3.
14. M.V. Berry, M. Tabor, Proc. R. Soc. Lond. A **349**, 101 (1976).
15. J. Mueller, J. Burgdoerfer, D.W. Noid, J. Chem. Phys. **103**, 4985 (1995).
16. K. Sohlberg, R.E. Tuzun, B.G. Sumpter, D.W. Noid, Phys. Rev. A **57**, 906 (1998).